

Oscillations of atomic nuclei in crystals

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Abstract

Oscillations of atomic nuclei in crystals are considered in this paper. It is shown that elastic nuclei oscillations relatively electron envelops (inherent, I-oscillations) and waves of such oscillations can exist in crystals at adiabatic condition. The types and energy quantums of I-oscillations for different atoms are determined. In this connection the adiabatic crystal model is offered. Each atom in the adiabatic model is submitted as I-oscillator whose stationary oscillatory terms are shown as deep energy levels in crystals. The I-oscillations can be created at the expense of recombination energy of electrons and holes on electron-vibrational centers in semiconductors. They interact among themselves, with phonons and electrons, they influence on physical properties of crystals and crystal structures. The I-oscillations representing oscillations of atomic nuclei relatively electron system in crystals or molecules are the important physical reality.

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I. INTRODUCTION

Electronic properties of crystals (and molecules) usually investigate by using of approached solutions of Schrodinger equation. The important results of such investigations are properties of electronic system but the available information about energy quantum and types of nuclei oscillations are limited because of features of used adiabatic approximations. An information about crystal oscillations usually receive from the dynamic analysis of traditional crystal models in which atoms are replaced by physical points with masses of atoms. Such traditional models contradict adiabatic theories because nucleus and electron envelop of every atom in this model is one particle and adiabatic nucleus oscillations (relatively electron environment) are impossible. Information about nuclei oscillations which was received on basis of traditional crystal models is incomplete. At the same time the role of nuclei oscillations in various physical effects, such as phonon drag of electrons and hyperconductivity - superconductivity at room and at higher temperatures, is important. Scientific understanding of such physical effects is inconvenient without enough information about nuclei oscillations and interaction of these oscillations with electrons and phonons. In this connection it is useful to consider the nuclei oscillations in crystals in accordance with adiabatic theory of solids, to construct the adiabatic crystal model in agreement with adiabatic theories, to estimate possible influence of nuclei oscillations on physical properties of crystals or molecules. Given paper is devoted to these questions.

II. THEORETICAL PRECONDITIONS

The modern theory of solids contain the representation about atomic structure of substances and Schrodinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi. \quad (1)$$

Hamiltonian (H) for a crystal include the kinetic energy operators for nuclei (T_z) and for electrons (T_e), and also crystal potential (V):

$$H = T_z + T_e + V. \quad (2)$$

Crystal potential V usually include the operators of Coulomb interaction between electrons (V_e), between nuclei (V_z), and between electrons and nuclei (V_{ez}) : $V = V_e + V_z + V_{ez}$.

Solution of Eq. (1) is the wave function of a crystal $\Psi(r, R, t)$ where t - time, r and R designate degrees of freedom for electronic system and for nuclei system, accordingly. It is impossible to solve precisely the given equation dependent on huge amount of (more than 10^{23}) variables because of known fundamental and technical difficulties. Theory searches for the reasonable approached solutions of the Eq. (1) which would allow to calculate and to predict noticed on experience physical magnitudes, and crystals properties. In this connection apply an approached methods. So, division of variables in the Eq. (1) would allow to simplify the problem and to consider motion of electron system irrespective of nuclei system. In such case these systems would submit to micro-canonical distribution, and the exchange of energy between systems would be impossible, as though they were divided by adiabatic membrane. For the first time P. Dirac has applied separation of electronic and nuclear variables [1] and has presented wave function as $\Psi(r, R, t) = \phi(r, t) \cdot \chi(R, t)$. He show that, supposing the energy conservation, it is possible to replace the Eq. (1) by two equations for wave functions $\phi(r, t)$ and $\chi(R, t)$, which describe movements of electronic and nuclear systems of a crystal:

$$i\hbar \frac{\partial \phi}{\partial t} = - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 \phi + \left\{ \int dR \cdot \chi^*(R_I, t) \cdot V(r_i, R_I) \cdot \chi(R_I, t) \right\} \phi, \quad (3)$$

$$i\hbar \frac{\partial \chi}{\partial t} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \chi + \left\{ \int dr \cdot \phi(r_i, t) \cdot H_e(r_i, R_I) \cdot \phi(r_i, t) \right\} \chi, \quad (4)$$

where m - electron mass, M_I - mass of I-th nuclei, $V(r_i, R_I)$ - crystal potential and $H_e(r_i, R_I)$ - Hamiltonian of electron system. Coupled equations (3)-(4) introduce the basis of the time-dependent self-consistent field (TDSCF) method. One can see from the Eqs. (3)-(4) that the potential field, in which each system of particles move, depends on time and from results of averaging on coordinates of other system. In it the new quality consists which electrons get at the presence of nuclei. That is visible even on example of hydrogen atom, where proton and electron separately have coulomb fields, but in envelop of hydrogen atom the electron move in coulomb field of nucleus, and the nucleus move in a field of electronic shell, which have not coulomb field. The electronic envelops of atoms can unite among themselves, forming molecules and crystals but electrons outside of shells can not do that. So the electronic envelops represent new collective quality of electrons in atom but exact division of variables in the Eq. (1) cannot be carried out, and the problem about movement of nuclei system and

electron system in a crystal generally is self-consistent and nonadiabatic. Nevertheless adiabatic approximations are used. Born-Oppenheimer adiabatic approximation [2] is related to the solution of the stationary Schrodinger equation

$$H\Psi = W\Psi, \quad (5)$$

where W - energy of a crystal. Wave function of a crystal is product of electronic and nuclear wave functions:

$$\Psi(r, R) = \varphi(r, R) \cdot \Phi(R). \quad (6)$$

One can receive from the equation Eq. (5) the following two equations

$$(T_e + V)\varphi(r, R) = E\varphi(r, R), \quad (7)$$

$$(T_z + E + A)\Phi(R) = W\Phi(R), \quad (8)$$

where E - energy of electron system and

$$A = - \sum_I (\hbar^2/2M_I) \int \varphi^*(r, R) \nabla_R^2 \varphi(r, R) \cdot d\tau_r \quad (9)$$

- adiabatic potential. Equations (7, 8) form the connected system because potential A includes dependence of electronic wave function from change of nuclei coordinates and crystal potential V depends from r and R . In it the reasons of unadiabatic interaction of electrons system with nuclei system consist. Potential A describe stationary and, hence, oscillating process of energy exchange between systems of electrons and nuclei. However adiabatic conditions are provided with the certain accuracy, if potential A is small or is equal to zero. The Eqs. (6-8) under condition of $A = 0$ are known as Born-Oppenheimer adiabatic approximation. The accuracy of the given approximation is determined by the contribution of potential A in energy of a crystal. The appropriate contribution of displacements, rotations and oscillations of nuclei system as a power series of small parameter $\eta = (m/M)^{1/4}$ was calculated in Ref. [2]. In accordance with [2] the energy of nuclei oscillations is proportional η^2 . In this connection sometimes assert, that the small magnitude of the relation (m/M) ostensibly is a condition of a validity for using of adiabatic approximation. This opinion is inexact, as the relation (m/M) is always small, but the validity of adiabatic approach depends on physical conditions and not always is justified. The wave function in Eqs. (6)

generally speaking differs from the exact solution and after her substitution in the Eqs. (5) the additional components turn out due to which the movements of nuclei are capable to cause electronic transitions and by that to break adiabatic condition. C. Herring has shown [3], that adiabatic approximation is correct, if

$$E_{ij} \gg \sum_{\nu} \hbar \omega_{\nu} R_{\nu} \int d^3 r \varphi_i^* \frac{\partial}{\partial R_{\nu}} \varphi_j, \quad (10)$$

where E_{ij} - energy of enabled electronic transition between conditions i and j, ν - number of oscillation modes for nuclei system, dR_{ν} - characteristic displacement of nuclei system at frequency with number ν . In case of crystals the systematic displacement and rotations of all system of nuclei can be excluded. It may to take into account only oscillations of nuclei at considering fixed crystal for estimation of adiabacity. Then in agreement with [4] the sufficient condition for validity of adiabatic approach on the only frequency with number ν is smallness of nuclei oscillations energy in comparison with E_{ij} :

$$E_{ij} \gg \hbar \omega_{\nu}. \quad (11)$$

Believing that the conditions Eqs. (10)-(11) are satisfied, sometimes, one apply additional approximation in which wave function of a crystal (for estimation of potential A and for calculation of energy for electronic system E) is product of independent from each other wave functions of electronic and nuclear systems:

$$\Psi(r, R) = \varphi(r, R_0) \cdot \Phi(R), \quad (12)$$

where R_0 - set of nuclei equilibrium positions.

Thus, the stationary oscillations of nuclei system are possible at adiabatic approximation conditions. Adiabatic oscillations of nuclei system do not depend on oscillations of electronic system. They do not influence electronic system and do not change electronic structure of a crystal as a whole. From the point of view of adiabatic theories the crystal lattice is formed by system of electrons, and the nuclei are placed in potential minima of electronic system, where they can carry out oscillations concerning electronic system. The opportunity of nuclei oscillations becomes a reality when the necessary energy is transmitted to them. These conditions can be executed, for example, with the help of the electron-vibrational centers (EVC). Adiabatic oscillations of nuclei are important but for the present time they are a poorly investigated type of oscillations in crystals and molecules.

III. OSCILLATIONS OF ATOMIC NUCLEI

Solutions of the Eqs. (7) and (8) in adiabatic approximation do not depend from each other. The analysis of nuclei system adiabatic oscillations may be carried out by analyzing the solutions of Eq. (8). This many particle problem about movements of nuclei system is possible to reduce, for example by Hartree method [5], to one particle problem about movement of one j-th nucleus in effective potential field $V(R_j)$ depending from coordinates only of j-th nucleus:

$$T_j + V(R_j)F_j = W_j F_j, \quad (13)$$

where T_j - operator of kinetic energy and F_j - wave function, W_j - energy of stationary oscillations of j-th nucleus in a potential field $V(R_j)$. This field is created by all electrons and nuclei of a crystal besides the j-th nucleus. The electronic environment of j-th atom brought basic contribution in $V(R_j)$. Contribution of electrons and nuclei from other atoms of a crystal is insignificant because of their symmetric and removed position concerning j-th atom nucleus. Adiabatic oscillations of nucleus occur on frequencies with number ν (which, generally speaking, differ from characteristic frequencies of electronic system oscillations) near to a minimum $V(R_j)$ conterminous with the center of atom electronic shell. They do not cause an electronic transitions and the electronic environment of each atom remains constant and motionless on frequencies with number ν . It is possible to name these oscillations as inherent or I-oscillations, because of their properties are determined by inherent parameters of atom: mass and charge of a nucleus, potential $V(R_j)$ near to the center of an electronic envelop.

Accordingly each atom in adiabatic models of a crystals should be presented as inherent oscillator (I-oscillator) consisting from a nucleus and electronic shell, which is connected with each other by elastic force. In such case unadiabatic processes are transitions between stationary conditions of adiabatic model. The electron-vibrational transitions caused by presence of potential A in the Eq. (8) are a typical example of unadiabatic processes in which I-oscillations of the electron-vibrational centers, electrons and phonons strongly interact among themselves. Thus the I-oscillator energy levels (I-terms) of the centers are shown as deep energy levels. Nuclei oscillations relatively electrons shells of atoms in crystal occur in small area ($\simeq 10^2 \text{ \AA}$) and in general they are necessary to research by quantum methods. Nevertheless in classical molecular dynamics the nuclei movements describe by Newtonian

equations of motion. If to study harmonic oscillations then it is suitable to use the known correspondence between results of quantum and classical theories. This correspondence consist in coinciding the transition frequency between adjacent quantum oscillatory levels of harmonic oscillator with his classical oscillation frequency. So energy spectrum of harmonic I-oscillations is possible to research by classical method. We used this possibility for description of oscillations in adiabatic crystal model when nuclei and electron envelops can move along straight axis U. Such diatomic model is shown in the top part of Fig. 1 where circles are electronic envelops and closed points in circles centers are nuclei of atoms. System equations of motion for this model may be written:

$$M_1 \frac{\partial^2}{\partial t^2} U'_{1n} = -b_1(U'_{1n} - U''_{1n}), \quad (14)$$

$$M_2 \frac{\partial^2}{\partial t^2} U'_{2n} = -b_2(U'_{2n} - U''_{2n}), \quad (15)$$

$$m_1 \frac{\partial^2}{\partial t^2} U''_{1n} = -b_1(U''_{1n} - U'_{1n}) - g_1(U''_{1n} - U''_{2n}) - g_2(U'_{1n} - U''_{1n-1}), \quad (16)$$

$$m_2 \frac{\partial^2}{\partial t^2} U''_{2n} = -b_2(U''_{2n} - U'_{2n}) - g_1(U''_{2n} - U''_{1n}) - g_2(U''_{2n} - U''_{1n+1}), \quad (17)$$

where M_1 and M_2 - nuclei masses, m_1 and m_2 - an electronic envelops fictitious masses, U' and U'' - displacements of nuclei and electronic shells from equilibrium position , b_1 , b_2 , g_1 , g_2 - coefficients of elastic forces, t - time, n - elementary cell number. If to be interested in waves of harmonical oscillations in a linear atomic chain consisting of atoms which differ only by factors g_1 and g_2 , it is necessary to put $m_1 = m_1 = m$, $M_1 = M_2 = M$, $b_1 = b_2 = b$. Let's accept for definiteness $g_1 > g_2$. Then the following dispersion relations are true:

$$\omega_{1,2,3,4}^2(q) = (D/2) \pm (D^2/4 - F)^{1/2}, \quad (18)$$

where $D = [M(b + g_1 + g_2 - C) - mb](mM)^{-1}$; $F = [b(g_1 + g_2 - B)](Mm)^{-1}$, $B = -[g_1 + g_2 + 2g_1g_2 - C]^{1/2}$, $C = 1 - 2 \sin(aq/2)$, q - wave vector, a - lattice spacing. The dispersive curves qualitatively are represented in Fig. 1 and contain known acoustic (A) and optical (O) branches, and also new branches (I) which concern to inherent oscillations representing oscillations of nuclei relatively electronic envelops. In this connection it is expedient to determine magnitudes of elementary quantums for I-oscillations. Nucleus of j-th atom (or

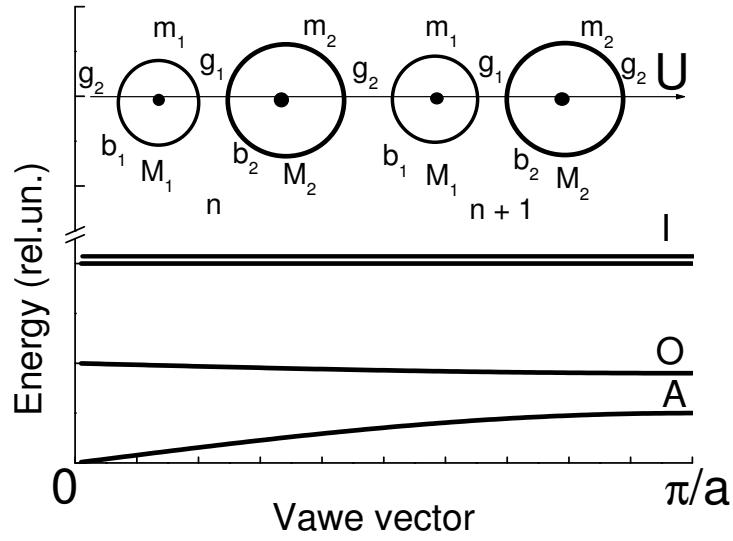


FIG. 1: Dispersive branches of acoustical (A), optical (O) and inherent (I) oscillations for linear two-nuclear chain according to Eq. (18). A fragment of such chain (cells with numbers n and $n+1$) is shown in the top part of the figure.

ion) of crystal oscillate in effective field $V(R_j)$. It is obvious that the basic contribution in $V(R_j)$ introduce the electrons from envelop of considered j -th atom but contribution of nuclei and electronic envelops both environments of the next and more distant atoms is insignificant because of their symmetric and distant location relatively of j -th atom. This feature together with deduction of adiabatic theory allow to calculate frequencies of nucleus I-oscillations in a field of his motionless electronic shell. The potential function $V(R_j)$ depends mainly on s-electrons density near the center of electronic envelop and in first approximation is spherical symmetric. Therefore small oscillations of nucleus near to the center of electronic envelop (α -type of I-oscillations) practically do not depend on polarization and have small unharmonicity. Quantums of I-oscillations in a crystal can be calculated when the function $V(R_j)$ is known. So, elementary quantum of harmonic inherent oscillations in statistical model of Thomas-Fermi atom does not depend on nuclear number and is equal to 0.43 eV. This energy can be considered as majorization of elementary quantum for I-oscillations in multi-electronic atom. Function $V(R_j)$ can be found for any atom from solving the Poisson equation with electrical charge density created by electrons of envelop near to her center. In atom of hydrogen the electronic density is defined by wave function: $e|\Psi_{1s}|^2$,

where e - electron charge. The appropriate magnitude of quantum for harmonic inherent oscillations $\hbar\omega_1 = 0.519$ eV. Un-harmonic correction to $\hbar\omega_1$ in the first and second orders of the perturbation theory in condition with oscillatory number $\nu = 0$ is equal to +7 meV (2.7 percent), in condition with $\nu = 1$ correction is equal to +35 meV (4.5 percent) and in a condition with $\nu = 2$ correction is equal to +70 meV (5.4 percent). The similar calculations for helium give magnitude of quantum $\hbar\omega_2 = 0.402$ eV. Electronic density near to the center of electron envelop in multi-electronic atoms is created basically by s - electrons. Quantums of inherent oscillations (α - type of I-oscillations) for atoms with numbers $Z > 80$ were calculated taking into account the s-conditions and the shielding a nuclei by electrons. Quantums of α - type I-oscillations for atoms with $Z > 2$ may be determined with help of the following formula

$$\hbar\omega_z = \hbar\omega_2 \left\{ \left(\frac{Z - 5/16 - \xi}{Z - 5/16} \right)^3 \cdot \frac{\Xi(Z - \xi)}{Z} \right\}^{1/2}, \quad (19)$$

where $\Xi = 1.2$ takes into account the contribution in electronic density from 2s- and 3s- conditions, $\xi = \sigma Z^{1/3}$, magnitude σ changes from 1 up to 1,15 at increase Z from 2 up to 80. Various types of I-oscillations in a crystal connected to various parts of atoms are possible. At increasing Z the electronic density at the center of atom envelop is considerably increased when emerge s-electrons of L -, M -, N - orbitals. Therefore it is expedient to define frequencies of I-oscillations for atom parts distinguished by the contents s-electrons. So, the joint oscillations of a nucleus and L - electrons (nucleus and two 1s electrons) concerning other part of environment represent β -type I-oscillations. Elementary quantum of β -type I-oscillations may be calculated for atoms with $Z > 2$ with help of the Eq. (19) at $s = \sigma(Z - 2)^{1/3}$ and $\Xi = 0.2$. It is possible to calculate elementary quantum of γ - type I-oscillations representing joint oscillation of a nucleus, K - and L - orbitals concerning other part of an environment for atoms with $Z > 8$ with help of the Eq. (19) at $s = \sigma(Z - 8)^{1/3}$ and $\Xi = 0,056$. Thus it is possible to describe terms of I-oscillations $\alpha-$, $\beta-$ and $\gamma-$ types by the formula for harmonic oscillator

$$\hbar\omega_\nu = \hbar\omega_z(\nu + 1/2), \quad (20)$$

where oscillatory quantum number $\nu = 0, 1, 2, \dots$ and $\hbar\omega_z$ is defined by the Eq. (19). These oscillatory energy levels together with the origin of energy scale $E = 0$ are energy levels of adiabatic crystal model and correspond to adiabatic ($\alpha-$, $\beta-$, $\gamma-$ type) nuclei oscillations

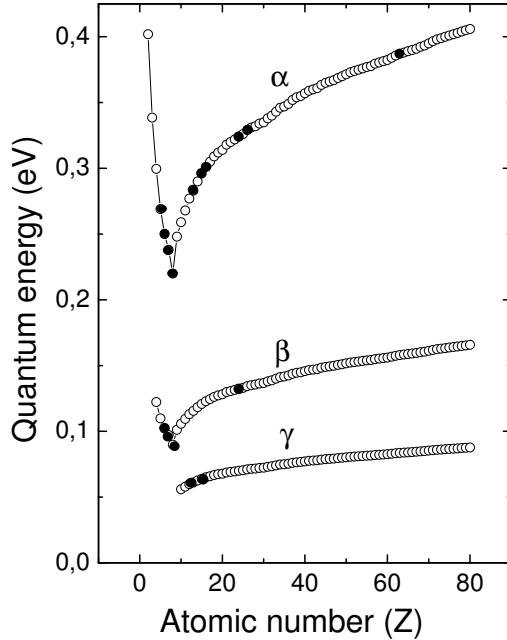


FIG. 2: Calculated dependencies of the elementary quantum energies for I-oscillations of α -type (α), of β -type (β), and of γ -type (γ) from atomic number Z are shown by open points. Experimental quantum energies of I-oscillations for several atoms are shown by closed points.

concerning electron system in a crystal. The transitions between the energy I-oscillatory levels or on the energy I-oscillatory levels occurring with electron and phonon participation are non-adiabatic processes which may be studied with the help of offered adiabatic crystal model. The calculated quantum meanings depending on Z are shown in Fig. 2 by open points for α -type, β -type, γ -type of I-oscillations. Experimental quantum meanings of I-oscillations for atoms: carbon, oxygen, sulfur, aluminium, iron, gadolinium, which were measured by various methods. They are shown in Fig. 2 by closed points.

IV. CREATION AND DESTRUCTION OF INHERENT OSCILLATIONS

Inherent oscillations can be created at the expense of suitable energy source for example thermal, optical, energy recombination in semiconductors. The thermal way is represented improbable, as the Debye temperatures for inherent α -type oscillations (more than 2500 K) exceed temperatures of melting for many materials. The way for excitation of I-oscillations at the expense of energy allocated at recombination in semiconductors probably is quite effective and practically important when recombination occurs on the electron-vibrational centers (EVC). The EVC in semiconductors usually represent an association of impurity atom with vacancy and are characterized by strong interaction of electrons with phonons. In the recombination act on such centers participate average $S > 1$ phonons, where S - constant for electron-phonon interaction (Pekar-Huang-Ryse constant) which can reach several tens. The EVC equilibrium positions may be changed at recombination. That promotes to excitation of I-oscillations. Thus, the oscillations terms of EVC are shown as deep energy levels. The I-oscillation of atomic nucleus can formally be characterized by temperature $T_\nu = \hbar\omega_\nu/k$, where k - Boltzmann constant. T_ν significantly exceed a temperature of a crystal lattice which are formed by electronic system. Or else, T_ν exceed temperature of electronic system. EVC disseminates this oscillatory energy in external environment with the greatest probability as crystal phonons, I-oscillations and waves of I-oscillations of the basic substance of a crystal. In result the recombination on EVC appears as the reason of I-oscillations and waves connected with phonons and capable influence on physical properties, of a crystal. Therefore it was possible to expect influence of EVC I-oscillations, and also I-oscillations of the basic substance atoms, on physical properties of semiconductor crystals and crystal structures.

V. DESCRIPTION OF EXPERIMENTS

In experiments were used flat polished semiconductor samples by thicknes 200 mkm containing EVC. It was GaP samples with impurities of aluminum or sulphur ($\simeq 5 \cdot 10^{15} cm^{-3}$): GaP(Al) and GaP(S). Such impurities were chosen because atoms Al and S have masses appreciably exceed mass of atom Ga. This advantages emergence EVC and generation of I-oscillations. In experiments also was used quartz samples which where cut out from a single

crystal lengthways normal to axis c, and also samples of pyrolytic graphite and carbon nanotube films on substrates which were fabricated by dispersion of graphite by electronic beam in vacuum [6]. Carbon nanotube films represent regular structures from carbon nanotube by diameter about ten nm and in length about 0.1 mkm guided lengthways normal to a surface of a substrate. Silicon samples with impurities of phosphorus ($\simeq 5 \cdot 10^{15} \text{ cm}^{-3}$) and oxygen ($\simeq 10^{18} \text{ cm}^{-3}$): Si(P, O) were used also. In Si samples EVC was formed by oxygen atoms (A-centers: associations of oxygen atoms with vacancy, S = 5 for A-centers). For performance of electrical measurements Au and Al contacts to samples were used with identical success. The contacts rendered by thermal dispersion of metals in vacuum. Temperature dependencies of electrical resistivity $\rho(T)$ of samples containing EVC were measured within the range from 77 K to 700 K by a method Van-der-Pau and by two sonde method. The experimental temperature dependencies of resistivity in various sites are described by the formula $\rho(T) = \exp(E_a/2kT)$. With the help of this formula were determined the activation energies (E_a) on various sites of experimental dependencies $\rho(T)$.

Infra-red reflection (IR) spectra connected with EVC were measured in the optical range from 15 mkm (83 meV) to 2 mkm (620 meV) at 300K. The angle between IR beam and flat surface of sample was equal to 45^0 . IR reflection spectra was analyzed on the basis of theory for reflection of classical charged harmonic oscillator [7, 8]. IR reflectivity of the oscillator

$$R_\omega = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (21)$$

is defined by a parameter of refraction (n) and absorption coefficient (k). They depend on oscillator frequency (Ω), frequency of crystal lattice oscillations (ω_L), coefficient of damping (θ), optical permittivity (ε_{opt}) and optical frequency (ω) :

$$n^2 - k^2 = \varepsilon_{opt} + \omega^2 \frac{\Omega^2 - \omega^2}{(\Omega^2 - \omega^2)^2 - \omega^2\theta^2}, \quad 2nk = \omega_L^2 \frac{\omega\theta}{(\Omega^2 - \omega^2)^2 + \omega^2\theta^2}. \quad (22)$$

The greatest meanings of R_ω are located between Ω and ω_L . Contour of the spectrum depends from ε_{opt} and θ . According to the quantum theory [9, 10] the experimental spectra of reflection was decomposed on components every of which fits spectrum for one oscillator by selecting parameters Ω , ω_L , ε_{opt} and θ . Thus the specified parameters were defined.

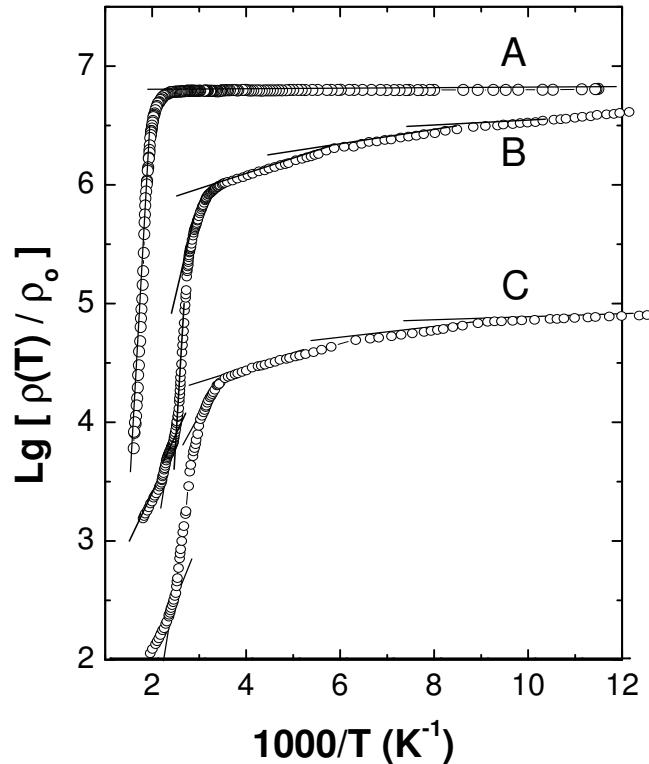


FIG. 3: Temperature dependencies of resistivity (ρ) for undoped single crystal GaP (A), for GaP doped by aluminium (B) and for GaP doped by sulphur (C) are shown by open circles. Straight lines show tangents to the linear curves sites.

VI. EXPERIMENTAL RESULTS AND DISCUSSION

A. Temperature dependence of resistivity

Typical temperature dependencies of electrical resistivity $\rho(T)$ for GaP samples are shown in Fig. 3. Magnitudes ρ_0 were selected for each curve that the curves were conveniently arranged in the Fig. 3. The sites of curves with constant inclinations are pointed out by pieces of line tangent to the curves. The inclination of lines tangents to the curves relatively axes of coordinates defines magnitudes E_a . Magnitudes E_a , measured at $T \leq 330$ K, are brought in Table I and basically correspond to known energies of phonons in GaP [11].

Energy of phonons are introduced in the central column in Table I. Other energies in Table I supposedly may be connected with I-oscillations (β - or γ -types) of Al or S and possible with combinations of such oscillations with phonons.

TABLE I: Activation energies for GaP(Al) and GaP(S) at $T < 330\text{ K}$.

| Activation energies E_a (meV) for GaP(Al) samples with numbers: | | | | | Phonons ^a in GaP (meV) | Activation energies E_a (meV) for GaP(S) samples with numbers: | | | | |
|--|------|------|------|------|---|---|------|------|------|------|
| 1 | 2 | 3 | 4 | 5 | | 6 | 7 | 8 | 9 | 10 |
| 8.1 | - | - | 7.2 | 8.0 | - | - | - | - | - | - |
| 15.0 | - | - | 14.8 | 14.5 | 14.25 | 15.0 | 14.8 | - | - | 14.3 |
| 24.5 | - | - | - | 25.0 | 24.42 | 24.0 | - | 24.6 | - | - |
| - | 35.0 | - | - | - | - | - | - | - | 28.0 | 28.0 |
| 45.0 | - | - | - | 44.6 | 44.75 | - | 42.0 | - | - | - |
| - | - | 49.0 | 48.0 | - | 47.00 | 47.0 | - | - | - | - |
| 75.0 | - | 83.0 | - | - | - | - | - | 70.0 | - | - |

^aReference [11]

The magnitudes E_a for GaP (Al) and GaP (S) measured at $T > 330\text{ K}$ are included in Table II. The Table II also contain energies calculated with help of Eq. (20) for inherent oscillations of Aluminum and Sulfur atoms with different ν . The energies was calculated with $\hbar\omega_{13} = 0.283\text{ eV}$ for Aluminum and $\hbar\omega_{16} = 0.301\text{ eV}$ for Sulfur which were determined in section III and pointed out in Fig. 2.

One can see from Table II that activation energies of samples with each type of impurities can be divided into two groups which corresponds to two columns dextral. One group consists of activation energies which are described by the Eq. (20). These activation energies are equal to energy of impurity atoms I-oscillations and correspond to transitions from oscillatory energy levels with $\nu = 0, 1, 2, \dots$ in the minimum of oscillatory potential where oscillatory energy $E = 0$. Such transitions for free quantum harmonic oscillator are forbidden but they are possible due to interaction of I-oscillator with crystal. Consequently, inherent oscillators of impurity atoms show duality of properties that can be explained by their interaction with the environment. Other group of energies in Table II consists of ones multiple $\hbar\omega_{13}$ for Al and $\hbar\omega_{16}$ for S. These groups of energies are also connected with inherent oscillations of impurity atoms and correspond to transitions between oscillator energy levels

TABLE II: Activation energies (eV) for GaP(Al) and GaP(S) at $T > 330$ K.

| E_a for GaP(Al) samples with numbers: | | | | | Calculated on Eqs. (20) | Multiple $\hbar\omega_{13}$ |
|--|------|------|-------|-------|----------------------------|--------------------------------|
| 1 | 2 | 3 | 4 | 5 | | |
| 0.14 | 0.14 | 0.14 | 0.138 | 0.137 | 0.142 ($\nu = 0$) | |
| 0.28 | 0.29 | 0.29 | 0.28 | 0.28 | - | $\hbar\omega_{13}$ |
| 0.42 | 0.42 | 0.43 | 0.42 | 0.43 | 0.425 ($\nu = 1$) | |
| - | 0.57 | - | 0.56 | 0.58 | | $2\hbar\omega_{13}$ |
| 0.71 | - | 0.72 | - | - | 0.707 ($\nu = 2$) | |
| - | - | - | 0.85 | - | | $3\hbar\omega_{13}$ |
| - | 0.97 | - | - | - | 0.991 ($\nu = 3$) | |
| 1.10 | - | - | - | 1.11 | | $4\hbar\omega_{13}$ |
| E_a for GaP(S) samples with numbers: | | | | | | Multiple $\hbar\omega_{16}$ |
| 6 | 7 | 8 | 9 | 10 | | |
| 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.151 ($\nu = 0$) | |
| 0.30 | 0.29 | 0.30 | 0.30 | 0.31 | | $\hbar\omega_{16}$ |
| 0.60 | - | 0.60 | 0.61 | - | | $2\hbar\omega_{16}$ |
| - | - | - | - | 0.74 | 0.753 ($\nu = 2$) | |
| - | - | 0.92 | - | - | | $3\hbar\omega_{16}$ |
| 1.03 | - | - | - | - | 1.050 ($\nu = 3$) | |

with different ν . One can see that $\hbar\omega_{13} = 0.283$ eV is the same in both groups of energies for Al impurity, and $\hbar\omega_{16} = 0.301$ eV is the same in both groups of energies for S impurity. Consequently, both groups of energies refer to the same type of centers that show classical and quantum properties (duality of properties).

The temperature dependencies $\rho(T)$ for pyrolytic graphite (PG) samples also are characterized by several activation energies. The magnitudes E_a for samples PG are submitted in Table III. They were measured at directions of a current parallel to nuclear planes (L)

TABLE III: Activation energies (eV) of resistivity for graphite samples at current directions parallel (L) or perpendicular (T) to atomic planes.

| Activation energies at L and T current directions and supposed type of oscillations (Type) | | | | | | | | | | Calculated on Eqs. (20) | Multiple $\hbar\omega_6$ |
|---|-------|-------|-------|-------|-------|-------|-------|------------|---------------------|----------------------------|-----------------------------|
| L | T | L | T | L | T | T | L | Type | - | - | |
| - | 0.004 | - | - | - | - | 0.003 | 0.004 | TA | - | - | |
| - | - | - | - | - | 0.006 | 0.006 | - | TO | - | - | |
| - | 0.029 | 0.021 | - | - | - | 0.024 | - | - | - | - | |
| 0.040 | 0.040 | - | - | - | - | - | - | TA | - | - | |
| - | 0.044 | - | - | 0.043 | - | - | 0.043 | TA | - | - | |
| - | - | - | - | - | - | 0.055 | - | TO | - | - | |
| 0.082 | - | 0.082 | 0.084 | - | 0.090 | - | - | LA | - | - | |
| 0.125 | - | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 | I_α | 0.125 ($\nu = 0$) | - | |
| 0.250 | 0.250 | 0.247 | 0.245 | - | 0.250 | 0.252 | 0.250 | I_α | - | $\hbar\omega_6$ | |
| - | - | - | - | - | 0.374 | - | - | I_α | 0.375 ($\nu = 1$) | - | |
| 0.500 | - | 0.507 | - | 0.500 | - | - | - | I_α | - | $2\hbar\omega_6$ | |
| - | - | - | - | - | - | 0.621 | 0.628 | I_α | 0.625 ($\nu = 2$) | - | |
| - | - | - | 0.759 | - | - | - | - | I_α | - | $3\hbar\omega_6$ | |

and perpendicular to nuclear planes (T) of graphite. Also in Table III the energies of I-oscillations for carbon are brought. They calculated with help of the Eq. (20) for various ν . These energies was calculated with $\hbar\omega_6 = 0.25$ eV for carbon which was determined in section III and pointed out in Fig. 2.

Top lines of Table III contain of energies which may be identified with phonons of graphite in the certain points of Brillouin zone appropriate to greater density of phonons. It is possible to explain energies 0.021 eV, 0.024 eV and 0.029 eV in Table III by a combination several acoustical phonons.

Activation energies located in the bottom of Table III can be divided into two groups. The first group consist of energies which close to energies calculated with help of Eq. (20). Second

TABLE IV: Activation energies (eV) for carbon nanotube films on quartz and fluorite substrates.

| Nanotube films on quartz substrates with numbers: | | | | | Nanotube films on fluorite substrates with numbers: | | | Calculated on Eq. (20) | Multiple $\hbar\omega_6$ |
|---|-------|-------|-------|-------|---|-------|-------|------------------------|--------------------------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | - | - |
| 0.013 | 0.012 | 0.013 | - | - | - | - | - | - | - |
| 0.017 | 0.017 | 0.017 | 0.017 | - | - | - | 0.016 | - | - |
| 0.030 | 0.032 | 0.030 | - | - | 0.029 | - | 0.035 | - | - |
| 0.040 | 0.050 | 0.040 | 0.037 | 0.043 | 0.044 | - | 0.056 | - | - |
| 0.095 | - | - | 0.067 | 0.095 | 0.086 | - | - | - | - |
| 0.127 | 0.125 | 0.125 | - | 0.128 | 0.121 | 0.125 | 0.125 | 0.125 ($\nu = 0$) | - |
| 0.027 | 0.250 | 0.250 | 0.250 | 0.248 | 0.250 | 0.250 | 0.250 | - | $\hbar\omega_6$ |
| - | 0.375 | - | - | - | - | 0.375 | - | 0.375 ($\nu = 1$) | - |
| - | - | - | 0.500 | 0.495 | - | 0.500 | 0.500 | - | $2\hbar\omega_6$ |
| - | - | - | - | - | - | 0.875 | - | 0.875 ($\nu = 3$) | - |

group consist of energies multiple E_0 . The activation energies may be explained as expense of energy in the acts of charge carriers generation at transition EVC from a condition with $\nu = 0, 1$ and 2 in minimum of potential $V(R_j)$ where oscillatory energy $E = 0$. Others energies are multiple E_0 and may be explained by transitions EVC between oscillatory condition with various ν . These results specify duality properties of carbon I-oscillator in graphite similar duality of properties for I-oscillators in GaP(Al) and GaP(S).

Experimental activation energies for carbon nanotube films on substrates are given in Table IV together with the calculated with help of the Eq. (20) data with subject to I-oscillator quantum of carbon atom ($\omega_6 = 0.25$ eV).

In the top lines of Table IV are located the energies measured at $T < 300 K$ which can be identified with phonons and their combinations. The bottom lines of Table IV contain the activation energies which were measured at $T > 300 K$. This energies can be divided into two groups. One group consist of the energies which close to calculated energies for carbon I-oscillations with help of Eq. (20). It gives the certain basis to connect them to transitions

of carbon I-oscillators from condition with $\nu = 0, 1, 2, 3$ in a condition with oscillatory energy $E = 0$. Other group consist of energies multiple $\hbar\omega_6 = 0.25$ eV which can be connected with transitions of the same I-oscillators between oscillatory condition differing by ν on 1 or 2.

The results of measurements and analysis of activation energies in samples Si(P, O) are qualitatively identical to the stated results, but the activation energies at $T > 300 K$ close to energies of oxygen I-oscillations (in A-centers) at $\nu = 0, 1, 2, 3, 4$.

It is impossible to explain the experimental dependencies $\rho(T)$ with scattering of charge carriers by phonons at $T < 300 K$ since the scattering is capable to create an opposite effect to the observed effect of reducing resistance when increasing the temperature. We connect experimental activation energies with creation of free charge carriers at the expense of oscillations energy of EVC for example EVC created by atoms Al or S in GaP, by atoms C in graphite or in carbon nanotube films, and by atoms O (A-centers) in silicon. The coincidence of calculated and experimental activation energies at $T > 300 K$ allows us to connect them with I-oscillatory terms of impurity atoms forming EVC. These terms are shown as deep energy levels.

B. Infrared spectra

Typical spectrum of reflectivity change (dR) in GaP(Al) is shown in Fig. 4 by curve A. The dR caused by introduction of impurity atoms (Al) in GaP in concentration $\simeq 5 \cdot 10^{15} cm^{-3}$. According to the theory [9, 10] the given spectrum was decomposed into components, which in Fig. 4 are denoted as B, C, D, E. The sum of the calculated spectra B, C, D and E, coincides with the experimental spectrum A if energies $\hbar\omega_{Li}$ ($i = 1, 2, 3, 4$) coincide with energies of Al α -type I-oscillators: $0.5\hbar\omega_{13}, \hbar\omega_{13}, 1.5\hbar\omega_{13}, 2\hbar\omega_{13}; \hbar\omega_{13} = 0.283$ eV. It is possible to see from these data that Al I-oscillators show duality of properties because in optical transitions the energy level of "zero oscillations" ($0.5\hbar\omega_{13}$) is shown. It is possible to connect energy $\hbar\Omega = 61$ meV with γ -type of atom Al I-oscillations. The attenuation (θ) in I-oscillators is great: $(\theta/\Omega) = 0.09$. The best consent between experimental and calculated spectra is reached if $\varepsilon_{opt} = 2$ though for GaP $\varepsilon_{opt} = 8.457$ [12]. It may be the $\varepsilon_{opt} = 2$ is necessary to carry not to a crystal GaP, but only to EVC. Thus the section of photon capture by EVC can depend on wavelength of phonons cooperating with EVC. The similar results were received at research of EVC reflectivity spectra formed by impurity atoms of

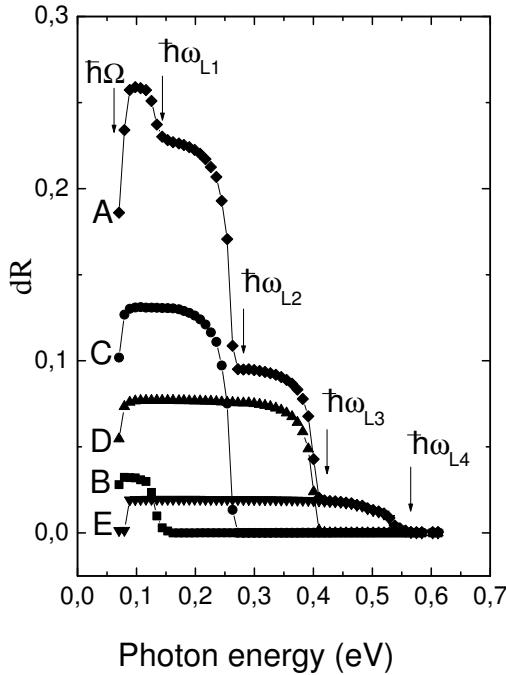


FIG. 4: Spectrum of reflectivity change (dR) which caused by impurity Al in GaP (A) and components of the spectrum connected with different I-oscillations of Al (B, C, D, E). Oscillator energy ($\hbar\Omega$) and energies of Al α -type I-oscillations in different oscillations states $\hbar\omega_{Li}$ ($i = 1, 2, 3, 4$) are shown by arrows.

sulfur for which $\hbar\omega_{16} = 0.301$ eV.

IR reflectivity spectrum of carbon nanotube film on molybdenum substrate (curve A) is shown in Fig. 5. Spectrum A was decomposed on reflection bands of two oscillators with energies: $\hbar\Omega = 60$ meV, $\hbar\omega_{L1} = 0.25$ eV and $\hbar\omega_{L2} = 0.375$ eV. The first of the energies is equal to elementary quantum of carbon β -type I-oscillations, second energy is equal to quantum of carbon atom α -type I-oscillations ($\hbar\omega_6$) and last of the energies is equal to carbon α -type I-oscillations at $\nu = 1$. Thus, the experimental data about interaction α - and β -types of I-oscillations and their influence on IR reflection spectra were received.

The typical reflectivity spectrum of carbon nanotube film on a copper substrate contains one band which is well described by the calculated reflectivity spectrum of oscillator with parameters $\hbar\Omega = 60$ meV and $\hbar\omega_L = 0,25$ eV which are accordingly equal to elementary

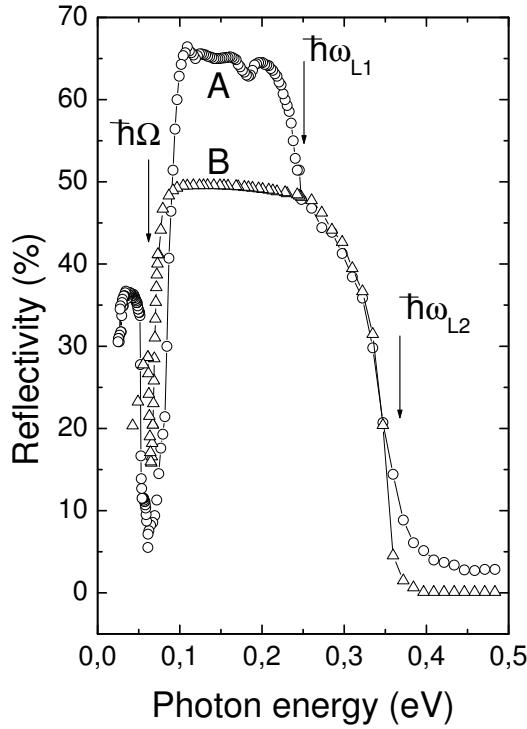


FIG. 5: Reflectivity spectrum of carbon nanotube film on molybdenum substrate (A) and calculated (at $\hbar\omega_{L2} = 0.375$ eV, $\nu = 1$) reflectivity spectrum for carbon α -type I-oscillator (B). Oscillator energy ($\hbar\Omega$) and energies of carbon α -type I-oscillations are shown by arrows.

quants β - and α -type I-oscillations of carbon atom.

Reflectivity spectrum of single-crystal quartz is shown in Fig. 6 (curve A). Curve B in Fig. 6 represents calculated reflectivity spectrum of oxygen α -type I-oscillator with the following parameters: $\hbar\Omega = 0.11$ eV; $(\omega_L/\Omega) = 0.25$ and $\varepsilon_{opt} = 1.2$, $(\theta/\Omega) = 0.011$. One can see that energy 0.11 eV is equal to $\hbar\omega_8/2$ at $\nu = 0$ in Eq. (20). Frequency ω_L can be identified with frequency of a phonon. The satisfactory consent of spectra A and B in a Fig. 6 confirms the electron-vibrational nature of the given reflection band and allows definitely to connect her with excitation of α -type I-oscillations of oxygen atom at $\nu = 0$. Some distinction of spectra A and B is explained by the contribution to reflection a components with $\omega_L = 2\Omega$ and $\omega_L = 3\Omega$.

Typical experimental reflectivity spectra of carbon nanotube film on quartz substrate are submitted in Fig. 7 (curves A, B, C). Spectrum A is measured at once after cultivation

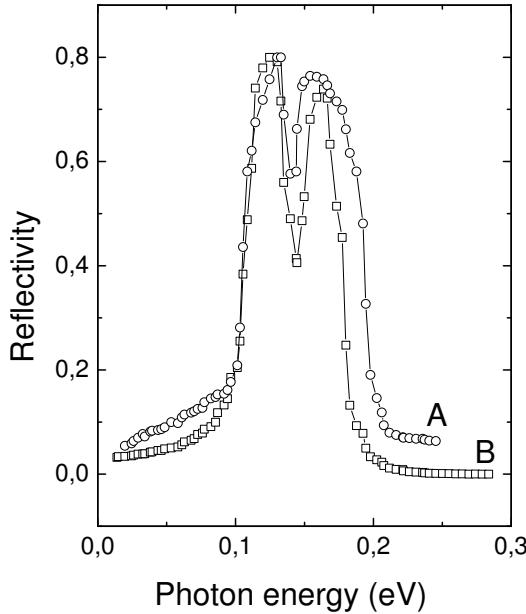


FIG. 6: Reflectivity spectrum of quartz (A) and calculated reflectivity spectrum of oxygen α -type I-oscillator (B).

of a film. Spectra B and C were measured 2 and 6 months later accordingly. Between measurements the film was stored at room conditions. The IR reflection factor (R_ω) increase considerably during a storage of samples. The similar changes of reflection spectrum for carbon nanotube film occur at her heating in vacuum. The changes of a spectrum occurring during two months of storage in room conditions can be achieved at heating of a samples in vacuum at $T \simeq 500$ K approximately within one hour. It allows to connect changes of the spectrum with changes of film structure. The experimental spectra contain a minimum in that area where the maximum of quartz reflection band is located. This reflection maximum is characteristic for impurity oxygen in silicon where it is displaced from 0.13 eV to 0.11 eV at increase of oxygen concentration and formation of quartz disseminations. This reflection maximum is characteristic also for silicon oxides, and for quartz. The reflection maximum definitely can be connected to α -type I-oscillations of oxygen atom at $\nu = 0$. Occurrence of reflection minimum close to 0.11 eV caused by carbon nanotube film on quartz substrate cannot be explained by anti-reflection coating action of a film because of the reflection minimum is observed at various thickness of a film and substrate. It is possible to explain

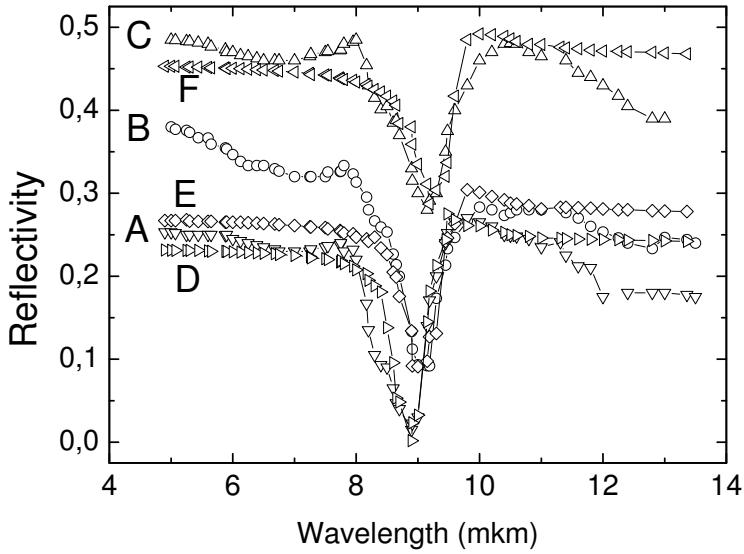


FIG. 7: Experimental reflectivity spectra of carbon nanotube film on quartz substrate after film fabrication (A), two month later fabrication (B), six months later fabrication (C) and reflectivity spectra of oxygen α -type I-oscillator (D, E, F), calculated at meanings of ϵ_{opt} equal to 2, 20, 250, accordingly.

this minimum by interaction between I-oscillators of oxygen atoms in quartz substrate and carbon atoms in nanotube film. Curves D, E, F in Fig. 7 represent spectra of oscillator reflectivity calculated at parameters $\hbar\Omega = 0.11$ eV and $\hbar\omega_L = 1.25$ eV with ϵ_{opt} equal to 2, 20 and 250 accordingly. The first from specified energies coincides with energy of α -type I-oscillations for oxygen atom at $\nu = 0$ in Eq. (20) ($\hbar\omega_8/2 = 0.11$ eV) but the second energy is multiple to elementary quantum of α -type I-oscillations for carbon atom ($\hbar\omega_6 = 0.25$ eV). The reflectivity spectra of nanotube films on quartz after thermal treatment are satisfactorily described by oscillator spectrum at $\epsilon_{opt} = 10^3 - 10^4$ but characteristic energy $\hbar\Omega = 0.11$ eV and $\hbar\omega_L = 1.25$ eV remain constant. It allows to explain the given experimental spectra by interaction with each other of oxygen and carbon I-oscillations at participation of phonons.

In silicon samples the IR reflectivity spectra, optical transmission and photoconductivity at electron-vibrational transitions on A - centers have phonon structure and are described by line Pekar-Huang-Rhyse spectra [13, 14]. Typical photoconductivity (curve A) and experimental spectra of IR transmission (curve B) for containing A-centers (10^{14} cm^{-3}) Si single-crystal are introduced in Fig. 8. Every of spectra lines correspond to participation

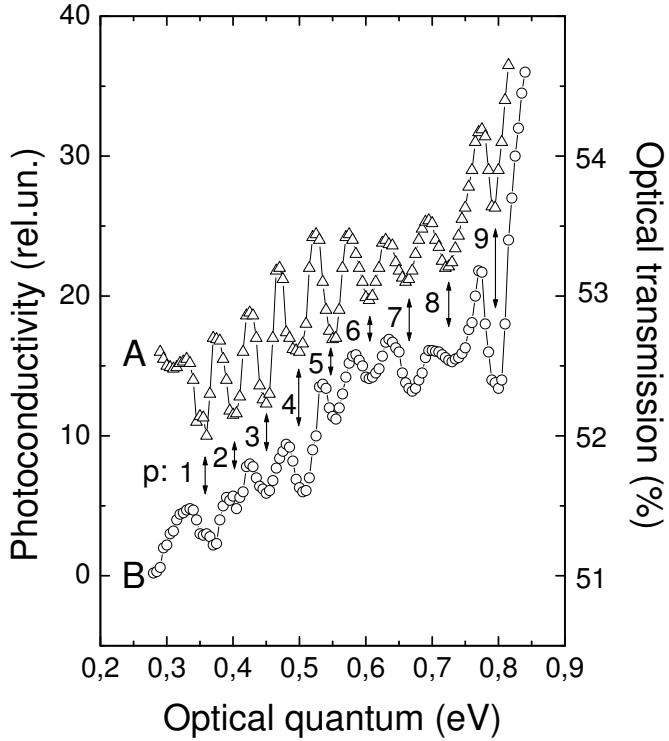


FIG. 8: Photoconductivity spectrum (A) and spectrum of IR transmission (B) measured at 80 K and connected with electron transitions on A-centers in silicon sample. Number of phonons which participate in electron-vibrational transitions is denoted as p.

of p phonons. The energies of electron transitions without phonons participation ($p = 0$) determined on basis of the theory [13, 14] coincide with energies of α - type oxygen atom I-oscillations counted from top of valence energy zone in silicon. These spectra are measured in polarized IR radiation when the IR electrical vector was directed as normal to [100] in a crystal. The spectra contain extremes which differ from each other on energies multiple energy of optical phonon in Si ($\simeq 55$ meV). Height of spectral lines follows dependence ($S^p/p!$), constant of electron-phonon interaction (Pekar-Huang-Rhyse constant) $S \approx 5$. Energy of electron transitions without phonons participation ($p = 0$) is close to energy $E_v + 0.33$ eV (where E_v - top of a valence energy zone) which correspond to $\nu = 1$ for oxygen α - type I-oscillator. At others polarizations of IR radiation it is possible to allocate spectra with participation others (optical and acoustic) phonons with the same meanings of constant S and energies of electron transition with $p = 0$ conterminous with I-oscillatory terms of

oxygen atom. Curve B in Fig. 8 represents typical for EVC spectrum of negative photoconductivity. Curve B in Fig. 8 represents spectrum of IR transmition. One can see that the increase of IR transmission (that is reduction of absorption) corresponds to photoconductivity increase. Thus terms of oxygen I-oscillations in A-center is similar to other atoms I-oscillations in structure EVC. The I-oscillation terms are shown as deep energy levels in semiconductors.

C. Discussion

Inherent oscillations of atomic nuclei relatively electron system (relatively electron envelops of atoms) in crystals and molecules exist that one can see from results of experimental and theoretical researches of different authors. The equations system Eqs. (14)-(17) at $n = 0$ describes oscillations of one crystal cell that is oscillations of appropriate molecule. In correspondence with Eq. (18) the oscillatory spectrum of a two-nuclear molecule contains frequencies of nuclei I-oscillations when electron envelops are motionless (on I-oscillations frequencies) and nuclei move relatively each other with inverse phase. Such oscillations really are available in spectra of two-nuclear molecules. F. Vilesov and M. Akopyan with help of optical mass spectrometry method investigated the ionization spectra for hundreds of molecules in various oscillatory conditions [15]. In particular they defined the energies of transitions from the adjacent oscillatory conditions in molecule of oxygen (O_2) whose differences are close to quantum of oxygen α -type I-oscillations (0.22 eV). That coordinates with I-oscillations presence in two-nuclear molecules.

G. Pastore and E. Smargiassi have applied in Ref. [16] Car-Parrinello [17] and Born-Oppenheimer [18] molecular dynamics for calculation model system consisted of eight silicon atoms forming the periodic diamond lattice. Car-Parrinello dynamic basically takes into account conditions with various meanings of oscillatory quantum number ν , but Born-Oppenheimer dynamic corresponds to the minimal oscillatory energy of a nucleus ($\nu = 0$). The comparison of application results for both dynamics allows to define transition energies between conditions with various meanings ν . In the Car-Parrinello dynamic "fictitious masses" about some hundreds of electron mass are used. They are inertia parameters assigned to every orbital degrees of electron freedom at a nucleus motion. It is obvious that fictitious mass of electron envelop in every atom sufficiently exceed mass of nucleus. There-

fore at movement of a nucleus the electronic envelop remain motionless and changeless. It corresponds to inverted adiabatic approximation (inverted in relation to well-known adiabatic approximations) when nuclei move (hot nuclei) but the electrons "do not heat up" systematically in the presence of the hot nuclei (cold electrons). It corresponds to the representation about massive and motionless electronic envelop (on frequencies of nucleus I-oscillations) which we used for definition energy quantums of I-oscillations.

In agreement with Ref. [16] the density of electronic conditions in considered atomic model system reaches the maximum near 1.3 eV that close to width of the forbidden zone in Si single crystal ($E_g = 1.16$ eV at temperature 0 K). The minimal energy in the calculated electron spectrum (0.6 eV) exceeds the maximal phonons energy ($\cong 55 \cdot 10^{-3}$ eV) that satisfies inequalities Eqs. (10)-(11) and does improbable systematical flow of energy between nuclei and electrons. The applicability of adiabatic approximation is thus reasonable. In [16] also are calculated: kinetic energy of the electrons (T_e), electronic energy (V_e), kinetic energy of nuclei (T_z), conserved energy ($E_{cons} = T_e + T_z + V_e$), physical total energy ($E_{phys} = E_{cons} - T_e$). Energies E_{cons} and E_{phys} are strictly constant. Energies V_e and T_e change on 0.43 eV and $0.81 \cdot 10^{-3}$ eV accordingly in opposite phase to each other with the common period $\tau_1 = 2.15 \cdot 10^{-14}$ s which correspond to energy $E_1 = (2\pi\hbar/\tau_1) = 0.194$ eV. The specified energy 0.43 eV can be connected to transitions of silicon I-oscillator between condition in minimum of potential $V(R_j)$ which coincide with oscillatory energy of nucleus $E = 0$ and condition with $\nu = 1$ that is calculated with help of Eq. (20) for silicon atom with meaning $\hbar\omega_{14} = 0.29$ eV. If it is correct then calculations in [16] proves observable on experience the duality properties of I-oscillators. In accordance with [16] the electron system acts on a nucleus by force which in Car-Parrinello approach (F_{CP}) and in Born-Oppenheimer approach (F_{BO}) oscillate in phase with the common period $\tau_2 = 4.32 \cdot 10^{-13}$ s which correspond to energy $E_2 = (2\pi\hbar/\tau_2) = 9.67 \cdot 10^{-3}$ eV. Besides, the difference ($F_{CP} - F_{BO}$) oscillate with two periods which correspond to energies $\cong 9.672 \cdot 10^{-3}$ eV and $\cong 0.2998$ eV. Last of these energies is near to energy of I-oscillator transitions for silicon atom between the adjacent oscillatory conditions with $\nu = 0$ (Born-Oppenheimer approach) and $\nu = 1$ (Car-Parrinello approach).

One can see from these results that in adiabatic approximation the complete crystal energy is constant but there is the oscillating process of energy exchange between system of electrons and system of nuclei. Therefore the adiabatic conditions Egs. (10)-(11) concerning

systems of electrons and nuclei is correct only for average energy on an time interval exceeding the periods τ_1 and τ_2 . The I-oscillations of atomic nuclei carry out important role in oscillating process of energy exchange between systems of electrons and nuclei in crystals. These I-oscillations give raise to such phenomena as phonon drag of electrons [19], thermal superconductivity, and hyperconductivity [20] at very high temperatures.

VII. CONCLUSION

Electronic envelop of any atom represents the new collective quality of electron system in comparison with quality of free electrons. The electronic envelopes of different atoms can unite with each other and form crystal lattices due to that the nuclei of atoms get an opportunity to carry out adiabatic inherent oscillations (I-oscillations) relatively electronic system of a crystal. In adiabatic approach there is no systematic energy flow from electronic system to nuclei system or in opposite direction. However there is the oscillating process of energy exchange between system of nuclei and system of electrons which is submitted by inherent oscillations in particular. These I-oscillations are a nucleus oscillations relatively motionless (on I-oscillation frequencies) nucleus environment in a crystal (α -type of I-oscillations). It can be also oscillations of a nucleus together with K-electrons (β -type of I-oscillations) or nucleus together with K- and L-electrons (γ -type of I-oscillations) relatively motionless (on frequency of I-oscillations) environment. Each atom in adiabatic model of crystal is submitted as appropriate I-oscillator. Non-adiabatic processes can be considered as transitions between stationary terms of I-oscillators.

Stationary I-oscillations and also waves of I-oscillations can exist in crystals. The energy spectrum of I-oscillations and waves of I-oscillations can be described by the formula for harmonic oscillator (at neglecting by non-harmonicity). The elementary quantum of harmonic I-oscillation depend on nuclear number, and for α -type I-oscillations they considerably exceed energy of phonons.

The effective creation of I-oscillations and waves of such oscillations can be carried out at the expense of recombination energy of electrons and holes on electron-vibrational centers in crystals. I-oscillations energy terms of the electron-vibrational centers are shown as deep energy levels in semiconductors.

The I-oscillations influence on physical properties of crystals and crystal structures. Thus

the inherent oscillations representing oscillations of atomic nuclei relatively electronic system in crystals or molecules are the important physical reality.

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